Pressure-Induced Metallization of the Mott Insulator MnO

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Abstract

High-pressure electrical conductivity experiments have been performed on the Mott insulator MnO to a maximum pressure of 106 GPa. We observe a steady decrease in resistivity to 90 GPa, followed by a large, rapid decrease by a factor of 10^5 between 90 and 106 GPa. Temperature cycling the sample at 87 and 106 GPa shows insulating and metallic behavior at these pressures, respectively. Our observations provide strong evidence for a pressure-induced Mott insulator-to-metal transition with an accompanying magnetic collapse beginning at 90 GPa.

Introduction

The electronic structures of the transition metal monoxides MnO, CoO, and NiO exhibit localization of their 3d electrons due to a combination of strong electron-electron correlation energies and narrow 3d electronic bands. Although one might expect the partially filled nature of the 3d electronic shells in these compounds to make them metallic, all of these transition metal monoxides are in fact robust Mott insulators due to correlation-induced localization of their charge carriers at the Fermi energy. The study of strongly correlated systems such as MnO is of interest because large electron-electron correlation effects are recognized to be important features of high-T_c superconductors[1], many magnetic systems[2] (e.g. heavy Fermions), and geophysically important materials in the Earth's interior.[3]

MnO is an antiferromagnetic ($T_N=122$K) ionic crystal with the B1 (rocksalt) structure at ambient conditions. The Mn^{2+} ions of this structure possess half-filled $3d^5$ shells, which form into a high-spin Hund's rule state of ^6S for a free ion. However, in the actual octahedral crystal field environment surrounding each Mn^{2+} ion in MnO, the 5-fold orbital degeneracy of the 3d level is partially lifted and the individual 3d states are split into triply degenerate t_{2g} and doubly degenerate e_g levels. Since this crystal field splitting for MnO ($\Delta E_{CF} \approx 1$eV) remains smaller than the Hund's rule exchange splitting ($\Delta E_{EX} \approx 4.5$eV), parallel electron spin alignment is favored, and the high-spin nature of the 3d electrons is retained. In this state, all of the parallel spin states of the t_{2g} and e_g levels are singly occupied, and the remaining, opposite spin states are completely empty ($^6A_{1g}$ crystal field ground state).

The degree to which a system will tend to exhibit correlation-induced Mott localization of electrons can be characterized by means of two parameters in the Hubbard model: (1) the Coulomb repulsion energy U for two electrons on the same atomic site; and, (2), the effective electronic bandwidth W. Mott localization is expected in narrow band systems when the ratio U/W exceeds a critical value. Many-body Monte Carlo simulations have predicted that this critical value is given by $\sqrt{N}$, or 2.24 for the d-band, where N is the orbital degeneracy.[3,4] For MnO at ambient pressure, the Hubbard U is about 7.8 eV and the effective bandwidth W is about

1 eV for a U/W ratio of 7.8, making MnO a strong Mott insulator.[3,5] Indeed, experimental values for the energy gap of MnO range from 3.8 to 4.2 eV[6,7] confirming that MnO is a wide-gap Mott insulator at zero pressure.[8]

Pressure Effects

The application of high pressure tends to increase the overlap between electronic wavefunctions and broadens the electronic bands, causing a decrease in the U/W ratio and the eventual delocalization of the electrons. High-pressure electrical conductivity experiments are an ideal method for observing the onset of delocalization, and have been recently used to study the metallization of the Mott insulators NiI_2, and Fe_2O_3 at 19 and 50 GPa respectively.[9,10]

In some cases, a metal-to-insulator transition may be accompanied by a structural transition. Previous experiments have demonstrated a similar sequence of structural transitions exists in several rock-salt-structured transition metal monoxides. In addition, recent first-principles calculations[3] have shown that for some transition metal monoxides, the requisite pressure for magnetic collapse and metallization could be as high as 230 GPa, and may indeed correspond to observed structural transitions. For MnO, previous high-pressure diamond anvil cell (DAC) x-ray diffraction studies have found that it undergoes a series of structural phase transformations with increasing pressure. The sequence B1(rocksalt) $\rightarrow$ distorted B1 $\rightarrow$ unidentified $\rightarrow$ B8(NiAs) was observed with transition pressures of 30, 90, and 120 GPa respectively.[11] Furthermore, Kondo et al.[11] reported that at pressure starting from around 80 GPa at room temperature, the MnO sample started to take on a metallic cluster, eventually becoming indistinguishable from the stainless steel gasket by 100 GPa. From this, they suggested that MnO is metallic above 90 GPa. Shockwave compression experiments on MnO have revealed that it undergoes an 8% volume collapse at a pressure of 90 GPa and an estimated temperature of 1000 °C on the shock Hugoniot P-V curve.[12] Electrical conductivity experiments on MnO under shock compression up to 50 GPa revealed no evidence of metallization to this pressure.[13] In addition, recent simulations predict magnetic collapse[3] in MnO at 149 GPa, and stabilization of the metallic B8(NiAs) phase[14] at pressures above 120 GPa. In order to confirm that MnO does indeed metallize under static pressure of around 1 Mbar, we performed high-pressure electrical conductivity experiments on MnO in a DAC to a maximum pressure of 106 GPa.

Experiment

We performed two *in situ* electrical conductivity experiments on MnO in a DAC, one to 90 GPa, and one to 106 GPa. MnO powder of 99.5% purity was obtained from Alfa Aesar, and loaded into a DAC (Kyowa Seisakusho Co. screw-type). The first experiment employed diamonds with 200-300 µm culet flats, while in the second experiment culet flats of 140 µm were used. In both cases, samples were loaded in pre-indented spring steel gaskets, and sample chambers of 100-110 and 75-80 µm were drilled for the first and second experiments respectively. No pressure medium was loaded in order to maximize sample volume and ensure good electrical contact. Ruby chips of 10-15 µm were loaded in each cell as a pressure marker (we denote the experiments using ruby as a pressure marker as Run1 and Run2a for the first and second experiment respectively); however, in the second run, pressures above 80 GPa were calculated by comparison of four x-ray diffraction spectra with the x-ray diffraction spectra and MnO equation-of-state (EOS) of Kondo et al.[11] (Run2b). By matching the positions of our

diffraction peaks to the corresponding diffraction peaks of Kondo et al., we were able to least-squares-fit each diffraction spectrum to a pressure, independent of crystal structure (since individual MnO peak positions are known as a function of ruby pressure[11], even though these peaks have not been indexed to an identified structure for 90GPa<P<120GPa). Energy dispersive x-ray diffraction was performed on beamline X-17C of the National Synchrotron Light Source, Brookhaven National Laboratory.

Electrical conductivity measurements were made via "designer" diamond anvils in each DAC. Designer diamond anvils are individually fabricated diamond anvils in which thin-film tungsten microprobes are encapsulated within a layer of high-quality, single-crystal, epitaxial diamond. Designer anvils have been fabricated for high-pressure electrical conductivity experiments as well as for magnetic susceptibility experiments.[15] Details of the fabrication of these anvils have been discussed elsewhere.[16,17] The designer anvil used in our experiment is shown in Figure 1. The eight microprobes are 10 μm wide and 0.5 μm thick, and are exposed only at the surface near the center of the diamond anvil's flat in order to make electrical contact with the MnO sample. Elsewhere, the electrical probes are covered by about 10-50 μm of epitaxial diamond, which serves to electrically insulate the microprobes from the metal gasket and also to protect them from damage due to shearing as the DAC is pressurized.

For large values of resistance (R>1k Ω), two-probe resistance measurements were made using a QuadTech 1865 Megohmmeter, while for smaller resistances (R<1k Ω) a four-probe technique was employed. The four-probe measurements were made by passing a DC current through a Keithley 2400 sourcemeter, with voltages measured via a Keithley 2182 Nanovoltmeter. Over a certain range of resistances in the vicinity of 1k Ω, both methods were used, enabling us to normalize the data from the two measurement techniques to each other. A closed cycle He cryostat (Cryomech ST15) was used to examine the temperature dependence of the resistance at specific pressures.

Results

In situ measurements of the sample resistance are summarized in Fig. 2. The initial sample is an opaque greenish-black powder that is insulating with a resistance on the order of 5x 10^8 Ω. Compression of the sample produces a gradual decrease in resistance to a value between 10^3 and 10^2 Ω at 80GPa. Slight variations in the rate of decrease in resistance appear to depend on sample preparation and geometry. Further compression in the range P>85GPa results in the rapid decrease of the resistance of the sample by five orders of magnitude, reaching a final value of 7-8x10^{-3} Ω at 106.4GPa. This resistance corresponds to an estimated resistivity of about 40 μΩ-cm, which is typical of a metal.

Figures 3 and 4 show the sample resistance versus temperature at 87 and 106GPa, respectively. At 87GPa (Fig. 3) the resistance behavior shows a large increase with decreasing temperature, indicative of thermal activation of carriers across a gap. The inset shows log(R) vs. 1/T, which gives an energy gap of 0.16eV, based on simple exponential behavior. The insulator to metal transition is complete by 106GPa, and the metallic behavior of the sample is clearly evident in Fig. 4, with dR/dT>0. In both cases, we attribute minor variations from linear (metallic) or exponential (insulating) behavior to slight changes in pressure with temperature.

Discussion

Our observation of a large, rapid drop in the resistivity of the Mott insulator MnO near 90 GPa strongly supports previous claims of metallization based on optical observations [11] and the disappearance of Raman peaks.[18] The onset of a rapid drop in resistivity at about 90 GPa coincides with the appearance of the unidentified intermediate phase reported by Kondo et al.[11] Since it has been predicted that the Mott insulator-to-metal transition of MnO is accompanied by a large volume collapse [3], and since the accumulated evidence for a Mott transition at 90 GPa is now very strong, we suggest that there may be a volume collapse at 90 GPa. From an examination of the EOS data of Kondo et al.[11], we conjecture that the $\Delta V/V_o$ magnitude of the volume collapse may be around 12%, although the actual structure of the phase immediately above 90 GPa has not yet been identified.

The decrease in the nearest neighbor distances of MnO with increasing pressures can be expected to have the effect of both increasing the amount of crystal field splitting (ΔE_{CF}) and increasing the effective (3d) bandwidth W. In the first case, if the crystal field splitting exceeds the Hund's rule exchange energy favoring the high-spin state, then the system may collapse to a low-spin state. In the second case, if the bandwidth W increases to the point that the U/W ratio becomes small enough (≈ 2.24 for d-band electrons), the system may then undergo a Mott insulator-to-metal transition. Either of these effects could conceivably result in the pressure-induced magnetic collapse of the high-spin state of MnO, although only the latter necessarily involves metallization. Based on generalized gradient approximation (GGA) calculations, Cohen et al.[3] have argued that the pressure-induced magnetic collapses of MnO, FeO, CoO, and NiO are all driven by broadening of the effective electronic bandwidth W and a Mott insulator-to-metal transition rather than an increase in crystal field splitting, which they claim is only a small effect. Our observation of a sharp metallic transition starting at 90 GPa is consistent with this view that an increase in bandwidth drives a magnetic collapse transition due to electron delocalization. We find, however, that the onset of metallization in MnO occurs at a pressure considerably below the predicted transition pressure of 149 GPa, which was based on the assumption of a B1 (rocksalt) structure for both the high-and low-spin phases.[3]

Conclusions

We have performed *in-situ* high-pressure electrical conductivity measurements on MnO to a maximum pressure of 106 GPa. Starting at 90 GPa, the resistivity undergoes a five order-of-magnitude drop, complete by 106 GPa. In addition, the insulating and metallic behavior of the MnO sample was confirmed upon temperature cycling at 87 and 106 GPa, respectively. Our observations strongly support a pressure-induced Mott insulator-to-metal transition with accompanying magnetic collapse in MnO beginning at a pressure of 90 GPa.

Acknowledgements

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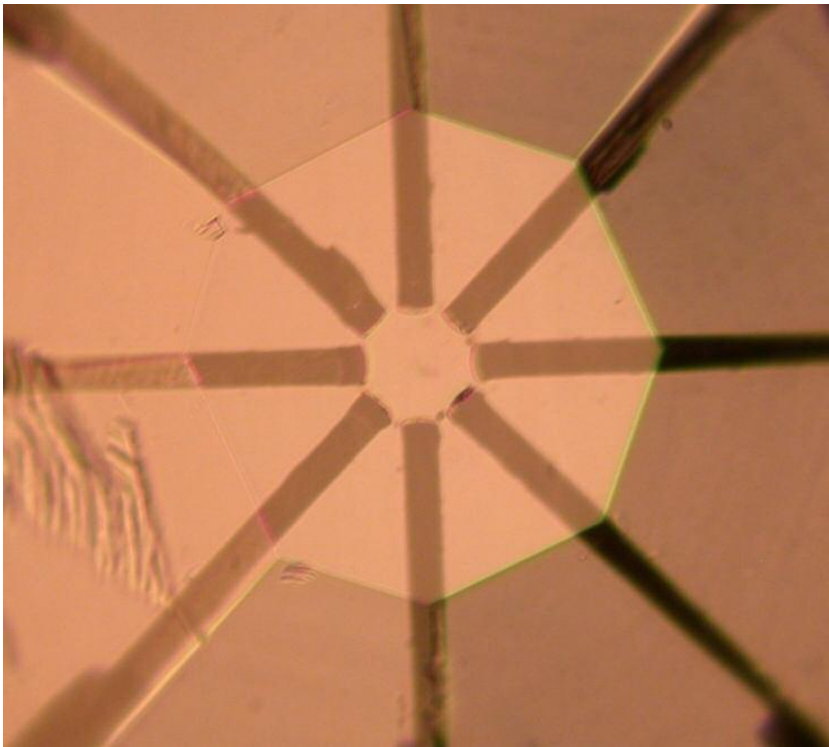
Captions

FIG. 1 Photograph of a designer diamond anvil used in conductivity experiments. The anvil was fabricated jointly at Lawrence Livermore National Laboratory and the University of Alabama at Birmingham. The flat size is approximately 140 µm and the linewidth of the probes is 10 µm.

FIG. 2 Resistance vs. pressure of MnO. Pressures were measured using ruby as an internal standard for Run 1 and Run 2a, while in Run 2b pressures were calculated by comparison with x-ray diffraction spectra. Temperature cycles A and B correspond Figs. 3 and 4 respectively.
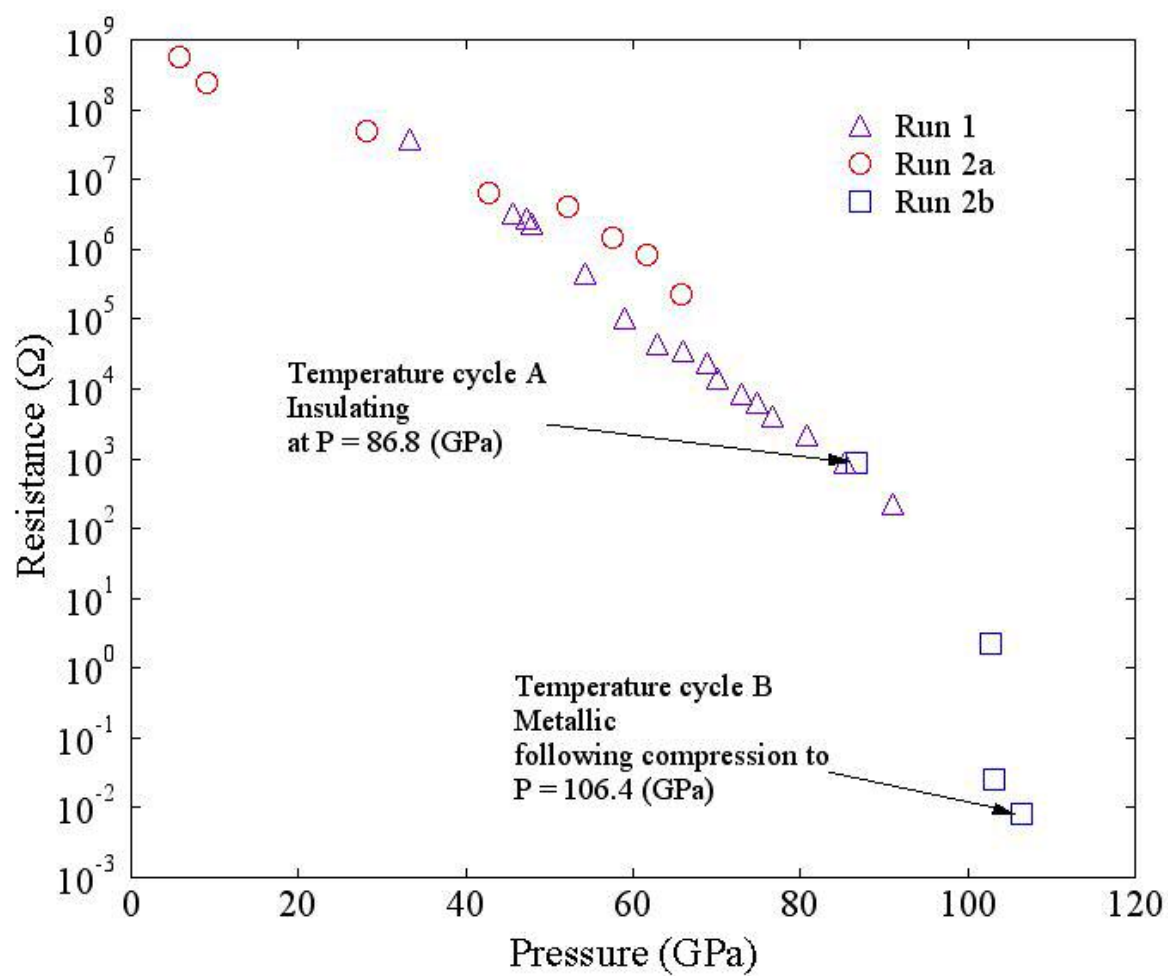
FIG. 3 Resistance vs. temperature upon cooling at 86.8 GPa. The sample shows insulating behavior commensurate with an effective gap of 0.16 eV.

FIG. 4 Metallic behavior of MnO. Resistance data were collected on cooling of the sample at 106.4 GPa.
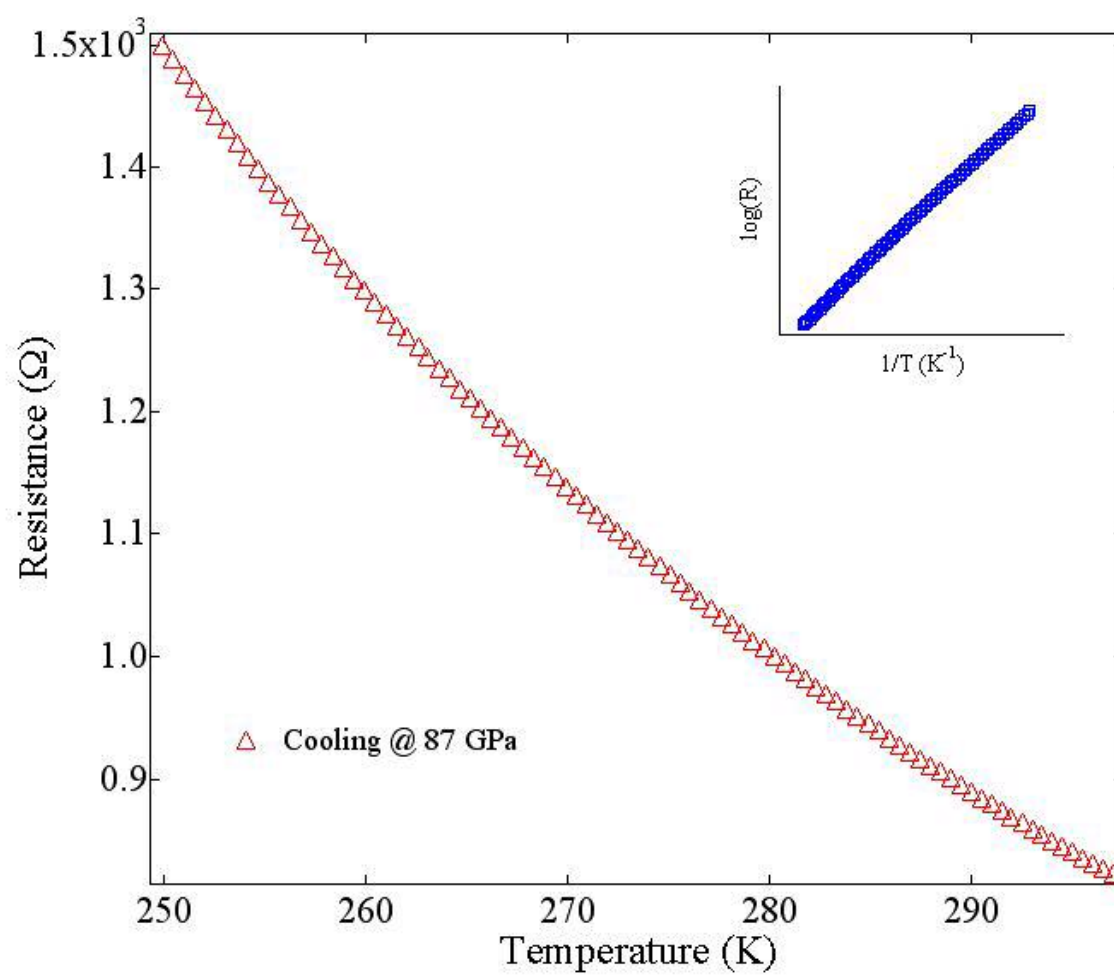
FIGURE1

FIGURE2

FIGURE3

FIGURE4